f_2 utilizing the constituent mobilities of the components, but wide discrepancies exist when the effects of interaction are not considered.

It seems possible, therefore, to predict rates of transport in systems of interacting components from the theory developed for non-interacting components.

Possible applications of this technique for the fractionation of certain systems of proteins are under investigation. One system to which it might be applied is a mixture of complete and incomplete antibodies, such as appears to be present in rabbit antisera to *p*-azophenylarsonic acid-conjugated proteins.[6] A suitable conjugated protein antigen could be used as the complexing agent for this system. In another direction, Morawetz and Hughes[14] have recently investigated the interaction of proteins with certain synthetic polyelectrolytes. These polyelectrolytes might find application as complexing agents in electrophoresis-convection fractionations.

[14] H. Morawetz and W. L. Hughes, Jr., *J. Phys. Chem.*, **56**, 64 (1952).

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Kinetics of the Formation of the Carbinol of Crystal Violet[1]

BY J. C. TURGEON[2] AND V. K. LAMER

RECEIVED APRIL 8, 1952

The fading of crystal violet in the presence of hydroxyl ion follows quantitatively the Brønsted–Debye law for primary kinetic salt effects. Crystal violet obeys Beer's law at the wave length of maximum absorption (590 mμ) in concentrations at and below 5×10^{-6} *M*. The activation energy for the reaction in water at 25° is 15.1 kcal/mole; the entropy of activation under these conditions is -12.3 cal./deg. mole. There is a strong specific solvent effect: the addition of acetone or dioxane to an aqueous solution of the dye produces a shift in the absorption peak of the crystal violet ion toward longer wave lengths and, at low concentrations of organic solvents, produces an effect on the specific reaction rate which is opposite to that expected on the basis of the decrease in dielectric constant. The use of normalized rate constants does not improve the agreement with simple electrostatic theory. The energy of activation in 40% acetone–water mixtures ($D = 59$) at $\mu = 0.005$ is 0.9 kcal./mole greater than in the case of water alone, at this ionic strength, contrary to the expected decrease due to the lowering of the coulombic activation energy in this reaction between oppositely charged ions produced by lowering the dielectric constant. The activation energy for the carbinol formation of malachite green is 0.7 kcal./mole less than that for crystal violet. The higher rate constant of the former (2.29 as against 0.28 liter/mole sec.) is due to reduction in activation energy, also to a less negative entropy of activation. The gas kinetic collision theory agrees with the observed rate for a probability factor $P = 0.098$ for $(r_a + r_b) = a_i = 2.49$ Å. *P* for the Debye theory (frequency of encounter, based on diffusion theory) is 0.84 for the reaction in water and 3.0 for the reaction in 40% acetone–water. An interaction between the crystal violet ion and the carbinol occurs which leads to spurious rate constants if the carbinol formation is slow ($t_{1/2} > 1$ hr.). Sufficient alkali was employed in these experiments to give reactions faster than this.

Introduction

Both rate and equilibrium studes[3-10] have been reported for the carbinol formation of the triphenylmethane dyes, as, for example, crystal violet (C.V., hexamethylpararosaniline), malachite green (M.G., 4,4'-bisdimethylaminotriphenylmethyl chloride), and brilliant green (B.G., the diethyl analog of malachite green). The absorption spectrum of the C.V. ion has been interpreted with regard to its structure by Lewis.[11] Figures 1 and 2 show the absorption spectrum of C.V. in water and various solvents. Biddle and Porter[7] worked with a solution of C.V. in a 6% alcohol–water mixture; they obtained a negative kinetic salt effect which they could not, of course, in 1915, interpret on the basis of modern electrolyte theory. Hochberg and LaMer,[3] using a conductimetric method, reported second-order constants (which were 25% higher than those of Biddle and Porter) for what they believed to be the homogeneous reaction

$$(\text{C.V.})^+ + {}^-\text{OH} \longrightarrow \text{carbinol}$$

Their data, however, indicate that half the initial amount of dye (5×10^{-3} mole/l.) had reacted with the NaOH before they obtained quantitative conformity with a second order kinetic law.

Shedlovsky, in a private communication to this Laboratory, reported[9] that he had been unable to obtain second-order constants for the fading reaction in water, using a spectrophotometer. He attributed his difficulty to the low solubility of the carbinol. Preliminary studies in the present investigation on C.V. showed that this dye indeed gave perceptible carbinol precipitation when the original dye concentration was of the order of 5×10^{-6} mole/l. in aqueous media.

Very recently, Laangvad[12] studied the alkaline fading of C.V.; his study of salt effects was over a limited range (< 0.02 *M*) and the precision of his measurements did not enable him to test unambiguously the limiting forms of the Brønsted–Debye equations for the velocity constant in the limit of zero ionic strength in terms of the energy and entropy of activation[13] given by Amis and La-

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[1] Abstracted from dissertation submitted by J. C. Turgeon to the Graduate Faculty of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1951.

[2] New York University Medical College, New York, N. Y.

[3] S. Hochberg and V. K. LaMer, THIS JOURNAL, **63**, 3110 (1941).

[4] A. Hantzsch and G. Osswald, *Ber.*, **33**, 278 (1900).

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[10] R. S. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949).

[11] G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **64**, 1774 (1942).

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Mer. The apparent discrepancy in behavior of the kinetics with regard to the dielectric constant of the medium,[7,3] and the strong possibility of previous work having been rendered inaccurate by the low solubility of the carbinol, indicate the necessity of reinvestigating the rate of carbinol formation of the triphenylmethane dyes.

Experimental Procedure

The crystal violet chloride (Allied Chemical and Dye Company product) was purified by precipitating the carbinol from an aqueous solution of the dye with excess NaOH followed by solution in hydrochloric acid and recrystallization from water as the crystal violet chloride. A stock solution 1.5×10^{-5} *M* in dye was prepared and stored in a paraffined flask. Carbonate-free NaOH solutions were standardized against Bureau of Standards potassium acid phthalate and stored in paraffined bottles equipped with soda-lime guard tubes.

The kinetic runs were made as follows: a volumetric flask filled to within 6 ml. of the mark with the reaction solvent to be used was brought to the temperature of the run in a thermostat. The dye (5 ml. of stock solution) was then introduced, the flask filled to the mark, its contents mixed and transferred to a paraffined florence flask, also in the thermostat, equipped with a soda-lime guard tube. Samples were removed from the flask at intervals and the dye concentration determined with a Beckman model DU spectrophotometer equipped with thermal jackets to maintain the temperature of the thermostat in the cell compartment. The 9.9-cm. glass transmission cells were rinsed with ethanol in between samples.

Dioxane, the commercial product (Eastman Kodak Company), was purified by refluxing with acid, then over sodium and distilling, according to the procedure of Hess and Frahm,[14] n^{25} 1.4205.

Acetone was purified by refluxing over calcium oxide and distilling, n^{25} 1.3565. The organic solvent-water mixtures were prepared for known weight per cent. of the organic solvent. The dielectric constants for the acetone–water[15] and dioxane-water[16] mixtures were obtained from the data of Åkerlof.

Adherence to Beer's Law.—Since crystal violet has been reported[17-19] to be one of a group of dyes that does not obey Beer's law, experiments were made on the optical density at the absorption maximum (5900 Å.) of more dilute ($<10^{-5}$ *M*) solutions of the dye than those previously investigated.[17-19] The intensity of the monochromatic light which is transmitted by an absorbing solution of thickness *l*, containing a concentration *c* of absorbing solute, is expressed by the Beer-Lambert law

$$I = I_0 e^{-cl\alpha} \quad (1)$$

where α is a constant for a given wave length, and I_0 and I refer to the original and transmitted intensities. This law does not hold if the molecules dissociate, associate, or in any way change their absorbing properties with change in concentration.

Table I shows that $\alpha = (1/cl) \log_{10} (I_0/I)$ is constant over the range 10^{-7} to 7.8×10^{-6} mole/l. at which point a 3% deviation from Beer's law appears. All kinetic experiments reported are for dye concentrations below 5×10^{-6} mole/l. where Beer's law is valid.

TABLE I

BEER'S LAW DATA FOR CRYSTAL VIOLET, λ = 590 mμ

10^6 concn., mole/l.	$\alpha = (1/cl \log_{10} I_0/I) \times 10^{-4}$, l. mole^{-1} cm.$^{-1}$	10^6 concn., mole/l.	$\alpha = (1/cl \log_{10} I_0/I) \times 10^{-4}$, l. mole^{-1} cm.$^{-1}$
11.4	8.30	0.98	8.56
7.80	8.34	.245	8.52
3.90	8.51	.122	8.42
1.96	8.46		

Average α below 7.8×10^{-6} *M* = 8.5×10^4 liters mole^{-1} cm.$^{-1}$

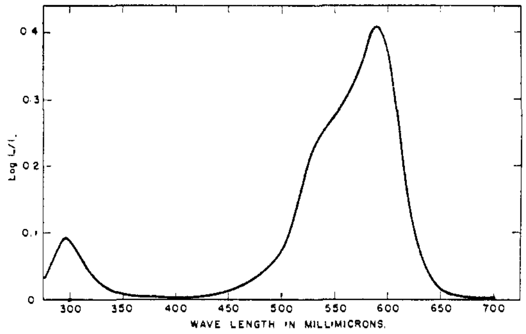

Fig. 1.—Absorption spectrum of 5×10^{-7} *M* C.V. in water.

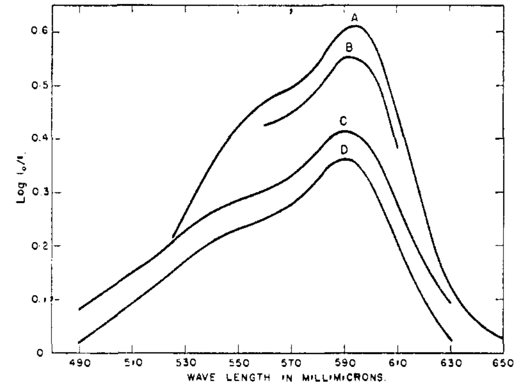

Fig. 2.—Curve A, absorption spectrum of 7×10^{-7} *M* C.V. in 40% dioxane; curve B, absorption spectrum of 6.5×10^{-7} *M* C.V. in 40% acetone; curve C, absorption spectrum of 4.9×10^{-7} *M* C.V. in 1.0 *M* KNO_3; curve D, absorption spectrum of 4.9×10^{-7} *M* C.V. in water (plotting increment = −0.05).

Interpretation of the Absorption Spectrum of Crystal Violet.—The G. N. Lewis[11] interpretation of the absorption spectrum of C.V. follows: the C.V. ion is similar to a three blade propeller and is not planar because the adjacent ortho hydrogens on the benzene rings have moved far enough from each other so that the force of repulsion is balanced by that which opposes free rotation of the rings about the bond joining them to the central carbon atom of the molecule. The "shoulder" of the absorption curve, on the lower wave length side of the maximum at 5900 Å. is attributed to a three blade propeller in which one blade is turned in an opposite sense from the other two.

Figure 1 shows the absorption spectrum of C.V. in water between 280 and 700 mμ, with the region between 490 and 630 mμ shown in detail in Fig. 2. It is seen in Fig. 2 that the absorption curve of C.V. is the same in water, 50% acetone-water, 40% dioxane-water and 1.0 *M* aqueous KNO_3, except for a displacement of the maxima from 590 mμ in water to 592 mμ in 50% acetone–water, and 594 mμ in 40% dioxane–water; and a lowering of the "shoulder" in these organic solvent-water mixtures.

The significance will be discussed later. Salts, up to 1.0 *M* KNO_3, exert no effect upon the absorption curve. The carbinol has an absorption maximum at 260 mμ.

Calculation of Rate Constants.—For a bimolecular reaction

$$(\mathrm{C.V.})^+ + {}^-\mathrm{OH} \longrightarrow \text{carbinol}$$

the rate of carbinol formation, dC_c/dt, or of disappearance of reactants

$$-\,dC_{(\mathrm{C.V.})^+}/dt = -\,dC_{\mathrm{OH}^-}/dt = dC_c/dt = k\,(C_{^-\mathrm{OH}})(C_{\mathrm{C.V.}^+})$$

where *k* is in liters/mole sec.

If $C_{\mathrm{OH}^-} \gg C_{\mathrm{C.V.}^+}$, then C_{OH^-} is constant, the reaction is first order in C.V., and

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(14) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Inc., New York, N. Y., 1941, p. 368.

(15) G. Åkerlof, THIS JOURNAL, **54**, 4125 (1932).

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(18) S. E. Sheppard and A. L. Geddes, THIS JOURNAL, **66**, 1995 (1944).

(19) L. Michaelis and S. Granick, *ibid.*, **67**, 1212 (1945).

$$k = \frac{2.3\ (\Delta \log C_{\mathrm{C.V.}})}{(\Delta t)(C_{\mathrm{OH}})} \frac{\text{liters}}{\text{mole sec.}} \qquad (2)$$

In the present investigation C_{OH} was $\geqslant 1000\ C_{\mathrm{C.V.}}$ so that it sufficed to follow only the variation of $C_{\mathrm{C.V.}}$ with time and know the initial C_{OH} to determine k.

Graph 3 shows the data for a typical run in water at 25°, with the ionic strength = 0.163.

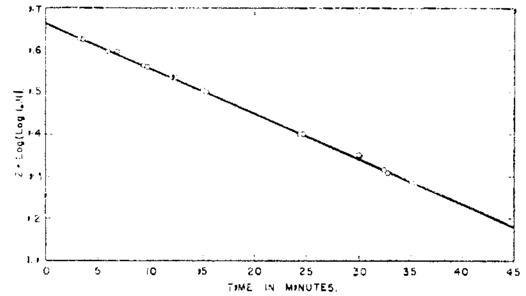

Fig. 3.—Data for a typical run: $2 + \log(\log I_0/I)$ *vs.* time in minutes.

The dye concentration employed was chosen so that the per cent. transmission of the solution lay in the range 30 to 70%, the region in which the spectrophotometer is most reliable.

Salt Effects.—For a reaction of the type

$$\mathrm{A}^{Z_{\mathrm{A}}} + \mathrm{B}^{Z_{\mathrm{B}}} = \mathrm{X}^{Z_{\mathrm{A}} + Z_{\mathrm{B}}} \longrightarrow \text{products}$$

where X is the critical or transition state and the superscript Z refers to the sign and number of electric charges on the ions, the molar rate constant k is given by the Brønsted–Christiansen–Scatchard equation for a double-sphere activated complex of radius

$$r = r_{\mathrm{a}} + r_{\mathrm{b}}$$

$$\ln k = \ln k_{\substack{\kappa = 0 \\ D = \infty}} - \frac{Z_{\mathrm{A}} Z_{\mathrm{B}} \epsilon^2 N}{DRTr} + \frac{Z_{\mathrm{A}} Z_{\mathrm{B}} \epsilon^2 N}{DRT} \times \frac{\kappa}{1 + \kappa a_{\mathrm{i}}} \qquad (5)$$

where $k_{\kappa = 0,\ D = \infty}$ is the molar rate constant for media of $\kappa = 0$; *i.e.*, zero ionic strength, extrapolated to a medium where $D = \infty$. The last term accounts for the Brønsted primary salt effect as a function of total salt concentration, and follows from the Debye–Hückel approximation for the potential of an ion against its ionic atmosphere.

For the reaction of C.V. with hydroxyl ion, for a constant D, with $Z_{\mathrm{A}} = +1$, and $Z_{\mathrm{B}} = -1$

$$\ln k = \text{const.} - \frac{\epsilon^2 N}{DRT} \times \frac{\kappa}{1 + \kappa a_{\mathrm{i}}}$$

where

$$\kappa^2 = \frac{8\pi N^2 \epsilon^2}{1000\ DRT} \mu$$

or

$$\log_{10} k = \text{const.} - \frac{A\sqrt{\mu}}{1 + \beta a_{\mathrm{i}} \sqrt{\mu}}$$

where $A = \epsilon^2 N\kappa/2.3\ DRT\ \sqrt{\mu}$, and $\beta = \kappa/\sqrt{\mu}$, and a_{i} is an ionic interaction parameter.[20] By use of the fundamental constants of Birge,[21] and the dielectric constant of water at various temperatures given by Wyman,[22] the values of A and β are given by

$$A = 1.018/(dt)^{3/2}$$

$$\beta = 0.3286 \times 10^8/(dt)^{1/2}$$

where

$$d = D/78.54,\ t = T^{(\mathrm{°K.})}/298.16$$

The dielectric constant-composition data of Åkerlof[15,16] were used in the computations. Table III gives the Debye–Hückel constants for the solvents employed in this investigation.

Provided that D and T remain constant, ln k should be a linear function of $\sqrt{\mu}/(1 + \beta a_{\mathrm{i}}\sqrt{\mu})$ for a suitable value of a_{i}. Graphs 4 through 7 show the salt effects studied; Table II lists the parameters, a_{i}.

TABLE II

DEBYE-HÜCKEL IONIC INTERACTION PARAMETER a_{i} FOR CRYSTAL VIOLET AND MALACHITE GREEN

Dye	Medium	Temp., °C.	D	a_{i}, Å.
C.V.	Water	25	78.54	2.49
C.V.	40% Acetone	25	59	4.72
M.G.	Water	25	78.54	2.80

TABLE III

DEBYE-HÜCKEL CONSTANTS FOR ORGANIC SOLVENT-WATER MIXTURES AT 25°

Vol. % Organic solvent	D	A	$\beta(10)^{-8}$
	Acetone–Water		
0	78.54	1.02	0.329
5	76	1.07	.334
10	74	1.11	.339
15	71.6	1.17	.344
20	69	1.24	.351
30	64.2	1.38	.364
40	59	1.56	.379
50	53	1.84	.40
	Dioxane–Water		
0	78.54	1.02	0.329
5	74	1.11	.339
10	69.3	1.23	.35
20	60.5	1.51	.374
30	51.6	1.91	.406

Since a_{i} is a parameter without too precise a physical meaning in a ternary system, one can only say from its much larger value in acetone–water mixtures that the C.V. ion is presumably solvated to a greater extent in this solvent than in water. It might not be going too far to say that there is probably an acetone molecule bound to the hydrophobic "faces"[18] of the C.V. ion in contrast to the hydrophilic groups at the end of the benzene rings which would be preferentially surrounded by water molecules. Since the $^-$OH ion approaches the central carbon atom from a direction perpendicular to the plane of the C.V. ion, the congregation of acetone molecules about the flat part of the ion would result in making the C.V. ion larger in its reaction with $^-$OH.

Solvent Effects.—According to quasi-equilibrium reaction rate theory

$$k = \gamma \frac{RT}{Nh} e^{-N\Delta F^{\ddagger}/RT} \qquad (7)$$

or

$$\ln k = \ln \gamma \frac{RT}{Nh} - \frac{N\Delta F^{\ddagger}}{RT}$$

where k is the bimolecular rate constant, N is the Avogadro number, R is the gas constant, and γ an unknown transmission factor equated to unity in the absence of methods for determining its value. On the basis of a double sphere activated complex of radius

$$r = (r_{\mathrm{A}} + r_{\mathrm{B}})$$

this may be written

$$\Delta F^{\ddagger} = \frac{RT}{N}\left(\ln \frac{RT}{Nh} - \ln k^{D = \infty}_{\kappa = 0}\right) + \frac{\epsilon^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{Dr} - \frac{\epsilon^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{D} \times \frac{\kappa}{1 + \kappa a_{\mathrm{i}}} \qquad (8)$$

($k^{D = \infty}_{\kappa = 0}$ is the molar rate constant in a medium of $D = \infty$, freed from the catalytic effect of ions of the surrounding atmosphere) where terms on the right-hand side correspond to $\Delta F_0^{\ddagger}$ for the reaction between neutral reactants, $\Delta F_{\mathrm{D}}^{\ddagger}$ for

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(20) V. K. LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

(21) R. T. Birge, *Rev. Modern Phys.*, **13**, 233 (1941).

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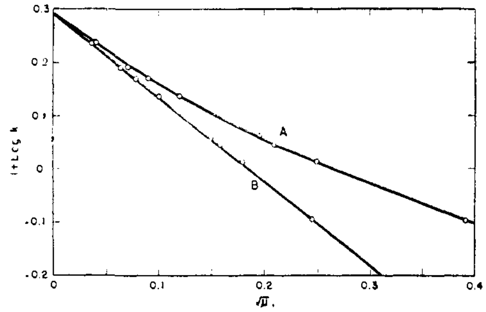

Fig. 4.—Salt effect data for C.V. in 40% acetone at 25°: curved line (A), 1 + log k vs. $\sqrt{\mu}$; straight line (B); 1 + log k vs. $\sqrt{\mu}/(1 + 1.56 \sqrt{\mu})$ as abscissa.

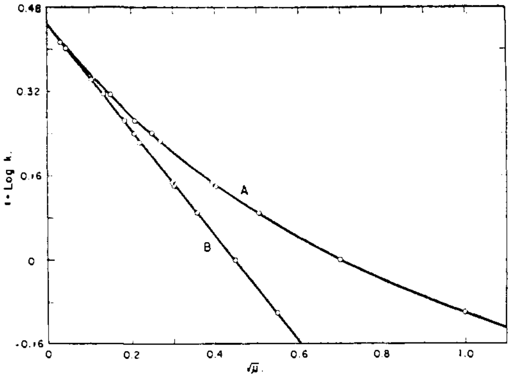

Fig. 5.—Salt effect data for C.V. in water at 25°: curved line (A); 1 + log k vs. $\sqrt{\mu}$; straight line (B); 1 + log k vs. $\sqrt{\mu}/(1 + 0.82 \sqrt{\mu})$ as abscissa.

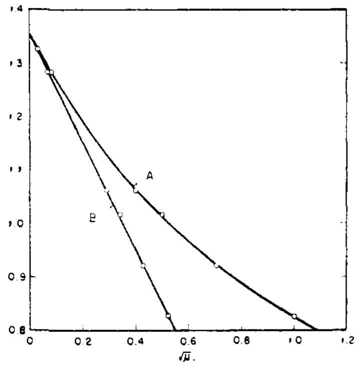

Fig. 6.—Salt effect data for M.G. in water at 25: curved line (A), 1 + log k vs. $\sqrt{\mu}$; straight line (B), 1 + log k vs. $\sqrt{\mu}/(1 + 0.92 \sqrt{\mu})$ as abscissa.

the effect of having a dielectric constant other than ∞, and $\Delta F_{\mu}^{\ddagger}$ for Debye–Hückel interactions. Thus

$$F_0^{\ddagger} = \frac{RT}{N}\left(\ln \frac{RT}{Nh} - \ln k^{D = \infty}_{\kappa = 0}\right) \text{ neutral reactants}$$

$$F_D^{\ddagger} = \frac{\epsilon^2 Z_A Z_B}{Dr} \text{ effect of dielectric}$$

$$F_{\mu}^{\ddagger} = -\frac{\epsilon^2 Z_A Z_B}{D} \times \frac{\kappa}{1 + \kappa a_i} \text{ ionic interaction}$$

To these must be added a non-electrostatic term, $\Delta F_S^{\ddagger}$ corresponding to the change in the free energy of the reacting species due to the presence of the medium other than that arising from changes in dielectric constant and ionic environment.[20]

In the case where $\Delta F_S^{\ddagger}$ (specific solvent) is negligible, and at zero ionic strength, at constant temperature k should depend only on the change in dielectric constant resulting from alteration of the solvent. Thus

$$\ln k_0 = \ln k_0{}^{D = \infty} - \frac{N\epsilon^2 Z_A Z_B}{DRTr} \qquad (9)$$

where the second term on the right is the kinetic counterpart of the Born equation for the work of transferring an ion from a medium where $D = \infty$ to the given medium, and r is the sum of the radii of the reactants and differs from a_i, the interaction parameter.

Numerically, for the reaction of $(C.V.)^+$ with hydroxyl ion

$$\frac{\Delta \log k_0}{\Delta(1/D)} = \frac{243}{r \text{ (in Å.)}} \qquad (10)$$

This predicts that, were solvation effects negligible, the addition of low dielectric constant solvent such as acetone or dioxane to the reaction solvent should result in an increase in the reaction rate constant k, the magnitude of the increase depending on $(r_A + r_B)$. The opposite is found to occur in the $(C.V.)^+ + {}^-OH$ reaction; this initial decrease in k upon lowering of dielectric constant is not due to the use of volume molar rate constants instead of the normalized mole fraction k^N.[23]

Calculation of k^N for acetone–water or dioxane–water mixtures according to the formula

$$k^N = k \times \frac{\Sigma(\text{moles/liter})_{\text{solvent}}}{\Sigma(\text{moles/liter})_{\text{standard}}} \qquad (11)$$

using water as the standard solvent results in values of k^N lower than k, since acetone and dioxane are both substances of larger molecular weight and molar volume than water. One would not expect the free energy change due to the change in van der Waals and other forces between the C.V. ion and the solvent molecules to be zero in going from water to an acetone–water mixture as a solvent; the crystal violet ion is a large organic molecule containing three benzene rings; there are three hydrophilic groups on the molecule, but even so the substance does not exhibit monomeric behavior in aqueous solution except at low concentration (~ 5 × 10^{-6} M). The solubility of the dye was found to be greater in 40% acetone–water mixtures than in water, showing the free energy of the dissolved substance to be less in the former solvent, despite its lower dielectric constant (59 as against 79). The minimum in the k_0–composition curve (Fig. 8) occurs at a lower mole fraction of dioxane than acetone, probably because of the lower dielectric constant of the former solvent; the addition of less dioxane is needed to make the effect of lowered dielectric constant counteract the specific solvent effects. Figure 9 shows log $k_{\kappa = 0}$ vs. $1/D$ for acetone–water, dioxane–water mixtures. The in-

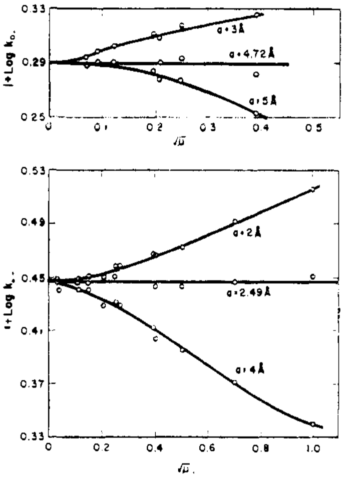

Fig. 7.—Effect of varying ionic parameter a_i on constancy of log $k_{K=0}$ = log k + $A \sqrt{\mu}/(1 + \beta a_i \sqrt{\mu})$. Top graph, data for C.V. in 40% acetone water at 25°: A = 1.56, β = 0.38 × 10^8; bottom graph, data for C.V. in water at 25°; A = 1.02, β = 0.329 × 10^8.

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[23] H. G. Davis and V. K. LaMer, *J. Chem. Phys.*, **10**, 585 (1942).

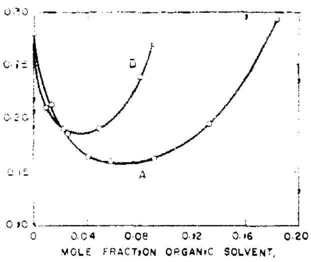

Fig. 8.—$k_{\kappa=0}$ *vs.* mole fraction organic solvent: curve A, data for acetone–water mixtures; curve D, data for dioxane–water mixtures.

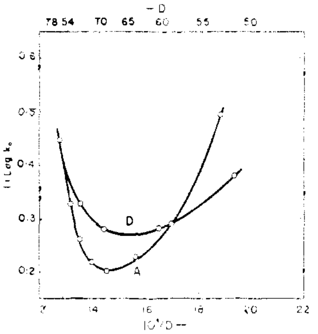

Fig. 9.—1 + log $k_{\kappa=0}$ *vs.* $1/D$ for various solvents: curve A, acetone–water mixtures; curve D, dioxane–water mixtures.

fluence of the addition of ethanol upon the rate is at first similar to the effect of adding acetone or dioxane; however, when the quantity of ethanol is greater than 10% by volume (3.2 mole %), there is a reaction of C.V. with the solvent (shown in Fig. 10 for 20% ethanol by volume), which makes interpretation of the data difficult. No work on this aspect was done beyond ascertaining the presence of this effect.

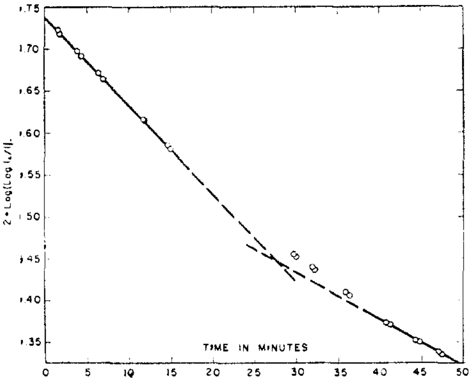

Fig. 10.—Data for run in 20% ethanol water. 2 + log (log I_0/I) *vs.* time in minutes.

Since the rate constants must be corrected to zero ionic strength and the work of Tomlinson[24a,b] has shown the difficulties in attempting to do this extrapolation in low dielectric solvents, k_0 was not computed for solvents of $D < 50$.

Effect of Temperature on Reaction Rate.—LaMer's[25] integration of the Arrhenius equation

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{\Delta E^{\ddagger}}{RT^2} \tag{12}$$

yields $\ln k = -(\Delta E^{\ddagger}/RT) + (\Delta S^{\ddagger}/R) + \ln \nu$ where ν is a frequency set[26] = to $\gamma \dfrac{RT}{Nh} e$ in Eyring's form of the theory.

The quantity $\Delta S^{\ddagger}$ then becomes the entropy of activation for all degrees of freedom; it will be convenient to separate it into an electrical and non-electrical part

$$\Delta S^{\ddagger} = \Delta S_0^{\ddagger} + (\Delta S_{\mathrm{D}}^{\ddagger} + \Delta S_{\mu}^{\ddagger})$$

where

$$\Delta S_{\mu}^{\ddagger} = -(\partial F_{\mu}^{\ddagger}/\partial T)_P$$

similarly for $\Delta S_0^{\ddagger}$ and $\Delta S_{\mathrm{D}}^{\ddagger}$. Since

$$\Delta F_{\mu}^{\ddagger} = -\frac{\epsilon^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{D} \times \frac{\kappa}{1 + \kappa a_{\mathrm{i}}} \tag{13}$$

and

$$\Delta F_{\mathrm{D}}^{\ddagger} = +\frac{\epsilon^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{Dr} \tag{14}$$

differentiation[27] yields

$$\Delta S_{\mu}^{\ddagger} = \frac{\Delta F_{\mu}^{\ddagger}}{T}\left[\frac{3}{2}\left(\frac{\partial \ln D}{\partial \ln T}\right)_P + \frac{1}{2}\left(\frac{\partial \ln V}{\partial \ln T}\right)_P + \frac{1}{2}\right] \tag{15}$$

which, for water at 25°

$$\Delta S_{\mu}^{\ddagger}/2.3R = 1.53\ Z_{\mathrm{A}} Z_{\mathrm{B}} \sqrt{\mu}$$

$$\Delta S_{\mathrm{D}}^{\ddagger} = \frac{\epsilon^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{rD^2}\left(\frac{\partial D}{\partial T}\right)_P = \frac{\Delta F_{\mathrm{D}}^{\ddagger}}{T}\left(\frac{\partial \ln D}{\partial \ln T}\right)_P \tag{16}$$

$$= -\frac{20 Z_{\mathrm{A}} Z_{\mathrm{B}}}{r \text{ in Å.}} \text{ cal./deg.-mole in water at 25°}$$

From the thermodynamic relation

$$H = \left[\frac{\partial(\bar{F}/T)}{\partial(1/T)}\right]_P$$

one gets

$$\Delta H_{\mu}^{\ddagger} = \Delta F_{\mu}^{\ddagger}\left[\frac{3}{2}\left(\frac{\partial \ln D}{\partial \ln T}\right)_P + \frac{1}{2}\left(\frac{\partial \ln V}{\partial \ln T}\right)_P + \frac{3}{2}\right] \tag{17}$$

For water at 25°

$$\Delta H_{\mu}^{\ddagger}/2.3RT = 0.52\ Z_{\mathrm{A}} Z_{\mathrm{B}} \sqrt{\mu}$$

Also, from the thermodynamic relation

$$\Delta H_{\mathrm{D}}^{\ddagger} = \Delta F_{\mathrm{D}}^{\ddagger} + T\Delta S_{\mathrm{D}}^{\ddagger}$$

one gets

$$\Delta H_{\mathrm{D}}^{\ddagger} = \frac{\epsilon^2 Z_{\mathrm{a}} Z_{\mathrm{b}}}{Dr} + \frac{\epsilon^2 Z_{\mathrm{a}} Z_{\mathrm{b}}}{Dr}\left(\frac{\partial \ln D}{\partial \ln T}\right)_P =$$

$$\Delta F_{\mathrm{D}}^{\ddagger}\left[1 + \left(\frac{\partial \ln D}{\partial \ln T}\right)_P\right] \tag{18}$$

If μ is kept constant, and the medium is varied so that the dielectric constant does not change with temperature, then

$$(\Delta H_{\mathrm{D}}^{\ddagger})_{\mathrm{D}} = -\frac{\epsilon^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{rD} + \frac{\epsilon^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{rD^2}$$

Accordingly, the Brønsted–Debye equation can be written

$$\log k = \left[\log \nu + \frac{\Delta S_0^{\ddagger}}{2.3R} + 1.53 Z_{\mathrm{A}} Z_{\mathrm{B}} \sqrt{\mu}\right] -$$

$$[E_0^{\ddagger}/2.3RT + 0.52 Z_{\mathrm{A}} Z_{\mathrm{B}} \sqrt{\bar{\mu}}] \tag{19}$$

It is seen from this equation that for ions of unlike sign, increasing μ decreases the activation energy, but also decreases $S^{\ddagger}$ more than proportionately, resulting in a decrease in rate.

Isocomposition and Isodielectric Solvents.—

$$\ln k_{\kappa=0} = f(D,T)$$

Differentiating with respect to T and multiplying by 2.3 RT^2

$$\Delta E_{0_{\mathrm{c}}}^{\ddagger} = \Delta E_{0_{\mathrm{D}}}^{\ddagger} + 2.3RT^2\left(\frac{\partial \log k_{\kappa=0}}{\partial D}\right)_T\left(\frac{\mathrm{d}D}{\mathrm{d}T}\right)$$

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[24] (a) H. Tomlinson, Ph.D. Dissertation, Columbia University, 1939; (b) F. G. Ciapetta and H. Tomlinson, *J. Phys. Colloid Chem.*, **55**, 429 (1951).

[25] V. K. LaMer, *J. Chem. Phys.*, **1**, 289 (1933).

[26] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941.

[27] V. K. LaMer and M. E. Kamner, THIS JOURNAL, **57**, 2662 (1935).

It has been shown that according to the Brønsted–Christiansen–Scatchard equation

$$\left(\frac{\partial \log k_{\kappa = 0}}{\partial D}\right)_T = \frac{\epsilon^2 Z_A Z_B N}{D^2 RTr}$$

provided no specific solvent effects exist. The existence of these for the carbinol formation of crystal violet unfortunately renders impossible the determination of $\Delta E^{\ddagger}_{\text{isodiel}}$ and $\Delta S^{\ddagger}_{\text{isodiel}}$.

The data in Tables IV and V are all for isocomposition media.

TABLE IV

ACTIVATION ENERGIES AND ENTROPIES FOR C.V.

Temp., °C.	Medium	μ	k	$E^{\ddagger}$, kcal.	$S^{\ddagger}$, cal./deg. mole
25	Water	0.0011	0.260		
35	Water	0.0011	.600	15.1	−12.3
40	Water	0.0011	.881		
25	Water	0.49	.100		
35	Water	0.49	.219	14.7	−15.7
40	Water	0.49	.332		
25	40% Acetone	0.005	.155		
35	40% Acetone	0.005	.379	16.0	−10
40	40% Acetone	0.005	.570		

TABLE V

ACTIVATION ENERGY AND ENTROPY FOR MALACHITE GREEN

Temp., °C.	Medium	μ	k	$E^{\ddagger}$, kcal.	$S^{\ddagger}$, cal./deg./mole
15	Water	0.005	0 820		
20	Water	0.005	1.26	14.4	−10.4
25	Water	0.005	1.93		
35	Water	0.005	4.22		

It is seen that this reaction obeys the equations for aqueous media

$$\Delta H^{\ddagger}_{\mu}/2.3RT = 0.52 Z_A Z_B \sqrt{\mu}$$

$$\Delta S^{\ddagger}_{\mu}/2.3R = 1.53 Z_A Z_B \sqrt{\mu}$$

$$E^{\ddagger}_{\mu = 0.49} - E^{\ddagger}_{\mu = 0} = -0.4 \text{ kcal./mole}$$

$$\Delta H^{\ddagger}_{\mu\text{theoret}} = -4.57 \times 0.7298 \times 0.52 = -0.49 \text{ kcal./mole}$$

$$\Delta S^{\ddagger}_{\mu = 0.49} - \Delta S^{\ddagger}_{\mu = 0} = -3.4 \text{ cal./deg. mole}$$

$$\Delta S^{\ddagger}_{\mu\text{theoret}} = -4.57 \times 1.53 \times 0.7 = -4.9 \text{ cal./deg. mole}$$

Neglecting κa_i in these calculations results in values of $\Delta H^{\ddagger}_{\mu\text{theoret.}}$ and $\Delta S^{\ddagger}_{\mu\text{theoret.}}$ too large by a factor of approximatively

$$(1 + \beta a_i \sqrt{\mu}) = 1 + (0.7)(0.82) = 1.57$$

The higher activation energy in acetone–water mixtures is consistent with a specific solvent effect resulting from the preferential solvation of the C.V. ion by an organic substance rather than water.

Comparison with Collision Theories.—According to theory, the rate of a bimolecular reaction is given by

$$PZ^0 e^{-\Delta E^{\ddagger}/RT}$$

Z^0 is the gas kinetic collision frequency for uncharged molecules and is given by

$$Z^0 = \frac{N n_a n_b}{1000} \sigma^2_{ab} \left[8\pi RT\left(\frac{1}{M_a} + \frac{1}{M_b}\right)\right]^{1/2}$$

where n_a and n_b are the concentrations of reactants in molecules/cc., σ_{ab} is the distance of approach between reactants for effective collision, M_a and M_b are the molecular weights of the reactants and P is referred to as the "probability" or "steric" factor. The rate constant k for ions of charge Z_a and Z_b is

$$k = PZ_i e^{-\Delta E^{\ddagger}/RT} \qquad (20)$$

where

$$Z_1 = Z_1^0/n_a n_b$$

and

$$Z_i^0 = Z^0\left(1 - \frac{Z_a Z_b \epsilon^2 LN}{DRr}\right) \qquad (21)$$

where

$$L = -\frac{\partial \ln D}{\partial T}$$

Since the factor PZ corresponds to $e\gamma\,(RT/Nh)\cdot\exp(\Delta S^{\ddagger}/R)$ of the absolute reaction rate theory, comparison of the two theories may be made by determining what value of P makes the two expressions equal, or by assuming $P = 1$, and determining what value of σ_{ab} gives agreement.[13]

For water at 25°, assuming $\sigma_{AB} = 2.5$ Å. (Debye–Hückel a_i) $P = 0.098$.

Debye[28a] (see also Umberger and LaMer[28b]) avoids the objections to using gas kinetic theory in solution and also the introduction of quantum theory for collisional processes by applying diffusion theory for evaluating the fundamental frequency factor which Smoluchowski first employed for the rate of coagulation of a colloidal suspension. He extended Smoluchowski's treatment to include the electrostatic effects arising from the presence of net charges, and arrives at the following formula for the number of encounters which includes the Brønsted primary salt effect as well as the Christiansen dielectric effect.

$$n\,\frac{8\,RT}{3\eta N}\left[\frac{2Z_1Z_2\epsilon^2N}{DRT(r_1 + r_2)} \Big/ \frac{2Z_1Z_2\epsilon^2N}{(e^{DRT(r_1 + r_2)} - 1)}\right] \qquad (22)$$

Here r_1 and r_2 are the radii of the reacting ions of charge Z_1 and Z_2, η is the viscosity of the medium, D, NR, T have the usual significance, ϵ is the electronic charge, and n is the number of molecules/cc. The factor in brackets results from Debye's treatment of electrostatic effects. If Z_1 and Z_2 are of the same sign, it is less than 1; if they are of opposite sign, it is greater than 1.

This approach has been re-examined recently by Christiansen.[29] At 298°K., with η for water $= 8.94 \times 10^{-3}$ dyne sec./cm.^{2},[30] and $(r_1 + r_2) = 2.5 \times 10^{-8}$ cm., one computes for the encounter frequency of equal sized uncharged molecules

$$\frac{8RT}{3\eta N}\,n = 7.39 \times 10^9 \text{ liters/mole sec.}$$

The electrostatic correction equals $-5.7/(e^{-5.7} - 1) = 5.7$, so the actual Debye encounter frequency factor in the present case should be

$$(7.39 \times 10^9)(5.71) = 4.22 \times 10^{10} \text{ liters/mole sec.}$$

This is larger than the observed frequency in the Arrhenius equation by a factor of only 1.2; this is excellent agreement for a model of this sort.

For 40% acetone–water, $\eta = 0.01365$ poise[31]

$$\frac{8RT}{3\eta N}\,n = 4.84 \times 10^9 \text{ liters/mole sec.}$$

With $D = 59$, the electrostatic factor in its simplest form becomes

$$-\frac{7.58}{e^{-7.58} - 1} = 7.6$$

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(28) (a) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); (b) J. Q. Umberger and V. K. LaMer, THIS JOURNAL, **67**, 1099 (1945).

(29) J. A. Christiansen, *J. Colloid Sci.*, **6**, 213 (1951).

(30) "Handbook of Chemistry and Physics," 31st ed., 1949, p. 1755.

(31) "International Critical Tables," **5**, 22 (1929).

and the frequency factor is

$$(7.6)(4.84 \times 10^9) = 3.67 \times 10^{10} \text{ liters/mole sec.}$$

This is smaller than the observed by a factor of 3.0. As Christiansen[29] points out, neither the gas collision mechanism nor the Debye encounter frequency furnish the rate determining term in a reaction of appreciable energy of activation as contrasted with a reaction of negligible energy of activation, for example quenching of fluorescence. If a collisional comparison is to be made, it would appear that Debye's encounter frequency is in better agreement with the data than the old gas collision value.

Equilibrium Studies.—The equilibrium constant K for the reaction

$$\text{carbinol} \rightleftarrows (\text{C.V.})^+ + {}^-\text{OH}$$

where

$$K = \frac{(\text{C.V.})^+({}^-\text{OH})}{\text{carbinol}}$$

and

$$\log K = p\text{H} - 14 + \log \frac{\alpha}{1 - \alpha}$$

where α = fraction carbinol ionized, was found to be $10^{-4.64}$ at 25° by Goldacre and Phillips.[8]

This gives as the free energy change for the ionization of the carbinol.

$$\Delta F^0 = -RT \ln K = (4.57)(298)(4.64) = 6.3 \text{ kcal.}$$

Adsorption.—At the start of the present investigation, it was observed that C.V. was adsorbed on glass—for instance, there was noticeable decrease in concentration of the solution in the absorption cell of the Beckman, especially the 1-cm. cells, after 5 minutes or so. In one experiment, a violet ring was observed to form about the inside of a beaker containing an aqueous solution of C.V. where a stirrer had scratched a band around the inside of the beaker. This blue ring persisted after the bulk solution had been decolorized with alkali, and could not be removed by rinsing with water; alcohol had to be employed. Gyani[32] found that tertiary basic nitrogen groups in organic dye molecules favor strong adsorption and that 80% of the initial dye in a C.V. solution was adsorbed on SiO_2 gel. This behavior of C.V. led to the use of paraffined vessels for the kinetic runs. The samples taken during a run were not left in the glass absorption cells long enough in the course of taking readings for the adsorption to occur.

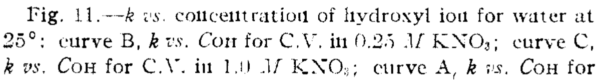

Fig. 11.—k *vs.* concentration of hydroxyl ion for water at 25°: curve B, k *vs.* C_{OH} for C.V. in 0.25 M KNO_3; curve C, k *vs.* C_{OH} for C.V. in 1.0 M KNO_3; curve A, k *vs.* C_{OH} for C.V., no added salt; curve D, k *vs.* C_{OH} data for M.G. (no added salt). 10

It was observed that at low alkali concentrations, $< 1 \times 10^{-3}$ M at 25°, the rate constant for the fading reaction was higher than it should be for a medium of that ionic strength, and that with 5×10^{-4} M $^-$OH, k was 10% higher than $k_{\mu = 0}$. Figure 11 shows this effect for M.G. (no added salt) and for C.V. at constant $\mu = 0.25$, and $\mu = 1.0$. Goldacre and Phillips[8] also had noted that at a pH below 11, the rate constant increased.

Their observation that benzene did not extract C.V. from neutral solutions of the dye (containing no carbinol), while if benzene were shaken up with a mixture of dye and carbinol, a blue coloration appeared in the benzene layer led to experiments being made on the dilute (7×10^{-7} M) dye solutions employed in this work to see if this adsorption of the dye by the carbinol also occurred there. Accordingly, a clear solution of C.V. carbinol made by adding alkali to 7×10^{-7} M dye was added to a C.V. solution, also 7×10^{-7} M, and the mixture shaken with benzene; the color was concentrated at the benzene–water interface, and eventually disappeared, even though at the pH of the water layer some of the colored ion should have remained.

A buffered (pH 9.3) solution of dye in a paraffined container will attain the equilibrium concentration of the colored ion in one day, and keep gradually fading until it becomes colorless in one month. In a glass bottle, a similar buffered solution becomes almost colorless overnight, while a deep coloration appears on the walls of the bottle. This coloration can only be removed by alcohol rinsings; water is ineffective, and the rinse alcohol solution has an absorption spectrum that shows a maximum at 584 mμ. A neutral solution of the dye in the same bottle does not show this behavior, adsorption occurs to a smaller extent and the rinsings give the same spectrum as the dye itself. Runs at low alkali concentration in 40% acetone–water mixtures, in which the carbinol is more soluble than in water, do not have abnormal rate constants. In water, runs with too high rate constants show an increase in rate as the reaction progresses. If the carbinol is originally present, then runs at alkali concentrations which give normal rates in the absence of carbinol are 8% faster than the normal value for that ionic strength and have the same rate constant as obtained by Hochberg,[1] using an original C. V. concentration 0.0033 M, once his reaction had attained second order conformity—*i.e.*, when it was half complete.

These observations indicate a complexing between dye and carbinol, this complex being more easily adsorbed on glass and concentrated at the benzene–water interface than the dye itself. With low ($<10^{-6}$) dye concentration and no carbinol present initially and sufficient alkali to produce a half-time of 50–60 minutes, the reaction is exclusively between dye and $^-$OH. With a low alkali concentration, so that the alkaline fading is slow, or a high alkali concentration and either carbinol present originally or a high C.V. concentration, then

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[32] B. P. Gyani, *J. Indian Chem. Soc., Ind. and News Ed.*, **13**, No. 1, 1 (1950); *C. A.*, **45**, 1837[i] (1951).

carbinol–dye interaction will have time to occur to a significant extent and abnormal rates will be observed. Figure 11, showing *k vs.* C_{-OH} data for M. G.,[33] and for C.V. with various salt concentrations, shows that deviations from normal behavior persist to higher alkali concentrations the greater the salt concentrations; *i.e.*, the lower the rate constant.

NEW YORK, N. Y.

(33) R. H. Dinegar, private communication, unpublished data.

[CONTRIBUTION FROM THE INSTITUTE FOR CHEMICAL RESEARCH, KYOTO UNIVERSITY]

Kinetics of Iodine-catalyzed Aromatic Bromination. I. A New Rate Expression

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Previous interpretations of data on the rate of the iodine-catalyzed bromination of aromatic derivatives are not satisfactory. The experimental data of Bruner have been recalculated through the use of a new expression for the rate law, in which it is assumed that the rate-determining step is the loss of hydrogen bromide from a 1:1 aromatic–bromine complex. This step is proportional in rate to some power, about three in the case of benzene, of the concentration of the BrI present. The new rate expression and mechanism account for both the iodine catalysis of the bromination and for the optimum rates observed with increasing amounts of iodine.

Detailed experimental data on the iodine-catalyzed bromination of benzene have been presented by Bruner.[1] Price[2] suggested that Bruner's measurements corresponded to the rate law

$$d[C_6H_5Br]/dt = k[C_6H_6][Br_2]^{3/2}[I_2]^{5/2} \qquad (A)$$

He assumed such higher order of the rate expression (A) might be due to some sequence of reactions involving, *e.g.*, $IBr_2^{(-)}$ or I_3Br.[3]

Suppose his mechanism were valid, but recalculation according to it leads to equation (B) instead of equation (A).

$$d[C_6H_5Br]/dt = k[C_6H_6][Br_2]^{3/2}[I_2]^{5/2}/[I_3^{(-)}]\ [I^{(+)}] \qquad (B)$$

In equation (B), $[Br_2]$ and $[I_2]$ should be the concentrations of free bromine and iodine, respectively. On the other hand, since Price calculated the experimental results taking the total unreacted bromide as $[Br_2]$, it is obvious that his $[Br_2]$ included not only free bromine but BrI, I_3Br and other bromides which appeared in his mechanism. As $[I_2]$, he took the total quantity of iodine added, but on account of large equilibrium constant for BrI formation there should remain only an extremely small quantity of free iodine when iodine was mixed with excess of bromine.

Further, according to equation (A) the greater the quantity of iodine used, the greater is the reaction rate; however, Bruner's data show an optimum in it. Iodine in excess of a given amount decreases the rate of reaction.

Robertson and his co-workers,[4] who used mesitylene as the reactant and carbon tetrachloride or chloroform as solvent, criticized Price's work and established other rate expressions. In order to account for the experimental results they assumed complicated successive and competing paths which involved the assumed existence of such complexes as Br_4, IBr_3, IBr_5 and I_2Br_4. Recently evidence has been presented in favor of 1:1 complexes between several halogens and a variety of benzene derivatives[5–9]; these are formed rapidly and equilibrium constants for their formation have been measured in some cases. The present paper presents a reinterpretation of Bruner's results, which is based upon a simple rate law and utilizes this new information as to the molecular species present in the reacting system.

Derivation of a New Rate Expression

As stated above, in a solution of bromine, iodine and an aromatic compound in an inert solvent, the following equilibria exist

$$Br_2 + I_2 \overset{K_1}{\rightleftarrows} 2BrI \qquad (1)$$

$$Br_2 + C_6H_6 \overset{K_2}{\rightleftarrows} C_6H_6{\cdot}Br_2 \qquad (2)$$

$$I_2 + C_6H_6 \overset{K_3}{\rightleftarrows} C_6H_6{\cdot}I_2 \qquad (3)$$

$$BrI + C_6H_6 \overset{K_4}{\rightleftarrows} C_6H_6{\cdot}BrI \qquad (4)$$

where K_1, K_2, K_3 and K_4 are equilibrium constants. As Robertson[4] has already indicated, the order of the rate law in aromatic bromination depends upon a number of factors, such as the nature of the aromatic derivative, the concentrations of the reagents and the solvent. He attributed this variation in order mainly to the differences in capacity for 1:1 complex formation of the aromatic ring against the halogen.[10]

In the present analysis, on the other hand, a single kind of aromatic–halogen complex (1:1) is assumed in accordance with the work cited above, and any requirement for higher orders probably referred to the process of removal of hydrogen bro-

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(1) L. Bruner, *Z. physik. Chem.*, **41**, 514 (1902).

(2) (a) C. C. Price, THIS JOURNAL, **58**, 1834, 2102 (1936); (b) C. C. Price and C. E. Arntzen, *ibid.*, **60**, 2835 (1938).

(3) C. C. Price, *Chem. Revs.*, **29**, 42 (1941).

(4) P. W. Robertson, J. E. Allan, K. N. Haldane and M. G. Simmers, *J. Chem. Soc.*, 933 (1949).

(5) F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948).

(6) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).

(7) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832, 3978 (1948); **71**, 2703 (1949).

(8) N. S. Bayliss, *Nature*, **163**, 764 (1949).

(9) (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **72**, 4677, 5170 (1950); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **73**, 462 (1951).

(10) Robertson assumed in his mechanism the 1:1 complex as an intermediate. But he considered that this complex was formed through the complicated successive reactions and the variation in order of the rate law was mainly attributed to these reactions.